Review

# Catalytic applications of red mud, an aluminium industry waste: A review

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## Abstract

Red mud is a by-product of bauxite processing through Bayer process. The amount of red mud generated depends largely on the type of ore used and the processing. Use of red mud as a catalyst can be a good alternative to the existing commercial catalysts. Its properties such as iron content in form of ferric oxide ($Fe_2O_3$), high surface area, sintering resistance, resistance to poisoning and low cost make it an attractive potential catalyst for many reactions. Besides red mud, ferric ion sludge from wastewater treatment plant has also been studied for its catalytic properties, mainly due to its ferric oxide constituent. This paper reviews the studies on red mud as a catalyst. The catalyst characteristics, reaction mechanisms involved and performance are examined and compared with iron oxide catalyst and commercial catalysts.

## Contents

## 1. Introduction

Noble metals and metal oxides are popular as catalyst for various industrial applications. In general, noble metals are more active in most of the catalytic reactions. However, they suffer from problems like high price, low stability, sintering, volatilization and poisoning [1]. Metal oxides are less active than the noble metals but their lower prices make them more desirable economically [2,3]. Moreover they are more resistant to poisons like arsenic, lead, phosphorous and halogens than noble metals [4]. Use of industrial waste or naturally occurring solids containing catalytically active metals like Fe, Ni, V etc. as a substitute to commercial catalysts can help reduce the cost associated with the use of catalyst. Red mud which mainly contains a mixture of oxides of Fe, Al, Ti and smaller amounts of Si, Ca and Na is a potential alternative catalyst at the commercial scale. Even after minor treatments it is still cheaper than both noble metals and metal oxides [1].

Red mud is generated as a waste during the processing of bauxite, the most common ore of aluminium. Bauxite was discovered by P. Berthier in 1821 in southern France and more

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than 68 years later, in 1889, Karl Josef Bayer invented the Bayer process for the production of alumina from bauxite [5]. Even more than a century later, the aluminium industries still widely rely on this process for alumina production [6]. The ore is washed, ground and dissolved in sodium hydroxide under heat and pressure. The resulting products are sodium aluminate liquor, that goes for further processing and a large quantity of un-dissolved solid waste called 'red mud' or 'bauxite waste'. Depending on the type/grade of ore used, the amount of red mud generated per tonne of alumina produced may vary from 0.3 tonnes for a high-grade ore to 2.5 tonnes for a low-grade ore [5]. After Australia, India occupies the second position in world's red mud generation that amounts to approximately 5.5 million tonnes annually [7]. The main problem created by this waste is due to its high alkalinity [5].

Red mud has been tested for various applications, which include:

- Water treatment: e.g. phenol removal from aqueous phase [8,9], heavy metal removal [10–24], nitrate removal [25], phosphate removal [26], dye colour removal [27,28] and for decontaminating acidic leachates [29];
- Soil and mine site remediation [30,31];
- Production of building and structural materials: e.g. cement [32–35] ceramic materials [36–40], casting components [41];
- Other uses viz. recovery of metals [42–45], pozollanic pigment production [46], treatment of gold ores [47], as a sorbent for $SO_2$ [48], as adsorbent for $H_2S$ from hot gases [49], hydrodechlorination [50], production of X-ray shielding materials [51], corrosion inhibitor for carbon steel [52].
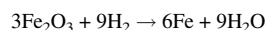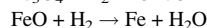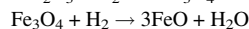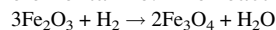
## 2. Physico-chemical properties of red mud

Red mud consists of a mixture of compounds originally present in the parent mineral and those introduced during the Bayer process. The main constituents of red mud include $Fe_2O_3$, $Al_2O_3$, $SiO_2$, $TiO_2$, $Na_2O$, $CaO$, $MgO$ and a number of minor constituents like K, Cr, V, Ni, Cu, Mn, Zn etc. [6,22,35,44,47,53,54]. Generally ferric oxide ($Fe_2O_3$) is the major constituent of red mud and gives it its characteristic brick red colour. The amount of red mud generated and its composition varies with the type and quality of ore used and the process parameters (Table 1 [10,12,14,16,19,20,27,29,31,32,34–39,41, 42,46,50,51,52,55–58]). The various mineralogical constituents identified in red mud by X-ray diffraction analysis are hematite ($\alpha$-$Fe_2O_3$), goethite (FeOOH), iron hydroxide (Fe(OH)$_3$), magnetite ($Fe_3O_4$), rutile ($TiO_2$), anatase ($TiO_2$), bayerite (Al(OH)$_3$), halloysite ($Al_2Si_2O_5(OH)_4$), boehmite (AlO(OH)), diaspore (AlO(OH)), gibbsite (Al(OH)$_3$), kaolinite ($Al_2Si_2O_5(OH)_4$), quartz ($SiO_2$), calcite ($CaCO_3$), perovskite ($CaTiO_3$), sodalite ($Na_2OAl_2O_3$ 1.68$SiO_2$ 1.73$H_2O$), cancrinite ($3NaAlSiO_4 \cdot NaOH$), whewellite ($CaC_2O_4 \cdot H_2O$), katoite ($Ca_3Al_2SiO_2(OH)_{12}$), gypsum ($CaSO_4 \cdot 2H_2O$) etc. [20,27,29, 44,59–62].

Red mud is highly alkaline with its pH ranging from 10 to 12 [22]. Because of its highly caustic nature it is considered hazardous to the environment, therefore necessitating neu-

tralization treatment [27,59]. Red mud has a fine particle size distribution [35,44] with 90% by volume below the size of 75 μm, and a high surface area [63]. The specific BET surface area of red mud generally lies between the range of 20–30 m$^2$/g. The specific surface area of hematite ranges from 3 to 5 m$^2$/g [62] depending on the method of preparation. However, the commercial $Fe_2O_3$ catalysts have higher surface area (e.g. 250 m$^2$/g for nanoparticles $Fe_2O_3$ catalyst [26], >50–100 m$^2$/g for a $Fe_2O_3$ (40–80%) based commercial catalyst [64]). The surface area of red mud can substantially be increased using some treatment methods (Table 2), which also result in the increase of the internal catalytic activity of red mud. These are discussed in the subsequent sections.

Ordóñez et al., conducted TPR (Temperature Programmed Reduction) studies on untreated red mud and lab prepared hematite (Fig. 1), and these were found to be similar to that of $Fe_2O_3$ [62]. The similarity in the TPR profile and stoichiometric values of red mud and hematite led to the observation that $Fe_2O_3$ is the only constituent of red mud that affects its reduction properties. TPR studies done on ferric oxide have demonstrated that $Fe_2O_3$ reduction takes place via $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$ [65,66]. The TPR profile shows two main peaks. The first peak appears at lower temperature (around 400 °C) corresponding to the reduction of $Fe_2O_3$ to $Fe_3O_4$. The second broader band appearing at a higher temperature (450–850 °C) consists of two unresolved peaks, corresponding to reduction of $Fe_3O_4$ to FeO and then to elemental Fe. The reaction scheme is as follows:

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$$
$$Fe_3O_4 + H_2 \rightarrow 3FeO + H_2O$$
$$FeO + H_2 \rightarrow Fe + H_2O$$

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$$3Fe_2O_3 + 9H_2 \rightarrow 6Fe + 9H_2O$$

## 3. Red mud as catalyst

Developing catalysts from waste materials is an effective means of value addition to the waste. Red mud has received considerable attention in this regard. This section discusses the various reactions involving the use of red mud as catalyst. Overviews of the efficiencies of some of these reactions are given in Table 3. These are discussed in details in the following sections.

### 3.1. Red mud as hydrogenation and liquefaction catalyst

Hydrogenation reactions involve the net addition of $H_2$, direct or indirect, usually to unsaturated organic compounds. The reaction between the compound and $H_2$ is carried out in the presence of a catalyst, which is required to activate the $H_2$. Red mud has been studied as a hydrogenation catalyst for coal [67,68], biomass [69], oil shale [70], certain organic compounds [71–75] and petroleum residues [76].

For coal hydrogenation and liquefaction, certain forms of mechanically mixed iron catalysts, red mud, iron ore, pyrites and pyrrhotite have been used in the past as well [77]. It was found that certain metallic oxides like red mud are not susceptible to catalyst poisons like sulfur and do not lose their

Table 1
Composition of red mud in various locations

| Area | Composition wt% | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | CaO | MgO | $K_2O$ | $Na_2O$ | L.O.I. | $V_2O_5$ | References |
| Seydiehir Aluminium Plant, Konya, Turkey | 2.50 | 14.10 | 38.30 | – | 4.10 | – | – | – | – | – | [10] |
| Etibank Seydiehir Aluminium Plant, Konya, Turkey | 15.74 | 20.39 | 36.94 | 4.98 | 2.23 | – | – | 10.10 | 8.19 | 0.05 | [12] |
| Hindustan Aluminium Company (HINDALCO) (Renukoot, India) | 9.64 | 17.28 | 38.80 | 18.80 | – | – | – | 6.86 | 7.34 | – | [14] |
| Queensland Alumina Ltd. refinery, Gladstone, Australia | 17.06 | 25.45 | 34.05 | 4.90 | 3.69 | 1.86 | 0.20 | 2.74 | – | – | [16] |
| Bauxite ore refinery, Guinea | 5.50 | 26.60 | 48.40 | – | 1.20 | 0.90 | – | – | 14.60 | – | [19] |
| Alumina-aluminio of san Ciprian, lugo, Spain | 6.10 | 20.10 | 31.80 | 22.60 | 4.78 | 0.20 | 0.03 | 4.70 | – | – | [20] |
| Slurry pond from the Worsley Alumina, Australia | 5.00 | 15.00 | 60.00 | 5.00 | – | – | – | 16.00 | – | – | [27] |
| Aluminium de Gréce S.A. | 6.96 | 15.65 | 45.58 | 7.07 | 14.84 | – | 0.07 | 3.26 | – | – | [29] |
| Eurallumina alumina plant, Italy | 9.58 | 17.19 | 30.45 | 8.61 | 7.77 | 0.86 | 0.30 | 12.06 | 12.38 | – | [31] |
| Aluminum de Grece | 6.80 | 19.95 | 40.80 | 5.80 | 12.60 | 0.20 | 0.14 | 2.70 | 10.54 | – | [32] |
| Shandong Aluminium Corporation, Shandong, China | 19.14 | 6.93 | 12.76 | 3.43 | 46.02 | 1.15 | 1.20 | 2.37 | 5.73 | – | [34] |
| Hindalco industries LTD. Renukoot | 3.00 | 48.00 | 16.50 | 8.50 | 0.50 | – | – | – | – | – | [35] |
| Shandong Province, China | 5.81 | 28.72 | 14.17 | 4.09 | 36.04 | – | – | 2.70 | – | – | [36] |
| Greece | 7.79 | 17.04 | 44.34 | 5.12 | 11.64 | 0.57 | 0.07 | 3.17 | 9.77 | | [37] |
| Seydiehir Aluminium Plant, Konya, Turkey | 12.08 | 23.29 | 35.73 | 4.08 | 2.81 | 0.76 | 0.28 | 7.40 | 8.66 | – | [38] |
| Eurallumina (Porto Vesme, Cagliari, Italy) | 11.60 | 20.00 | 35.20 | 9.20 | 6.70 | 0.40 | – | 7.50 | 7.30 | – | [39] |
| Alpart factory and the Alcan Ewarton red mud pond. Jamaica | 4.30 | 18.80 | 45.30 | 6.40 | 3.10 | – | – | 1.50 | – | – | [41] |
| Etibank Seydisehir Aluminium Plant, Turkey | 14.52 ± 0.37 | 18.71 ± 0.59 | 39.70 ± 0.67 | 4.90 ± 0.54 | 4.47 ± 0.56 | – | – | 8.82 ± 0.96 | – | – | [42] |
| Aluminium Pechiney, Gardanne, France | 4.98 | 15.00 | 26.62 | 15.76 | 22.21 | 0.95 | 0.02 | 1.02 | 12.10 | – | [46] |
| Ajka Aluminum Industry, Hungary | 9–15 | 16–18 | 33–48 | 4–6 | 0.5–3.5 | 0.3–1 | – | 8–12 | – | 0.2–0.3 | [50] |
| Hindustan Aluminum Company (HINDALCO) Renukoot, India | 8.50 | 20.10 | 31.88 | 21.20 | 2.99 | – | – | 6.00 | – | – | [51] |
| Seydisehir Aluminium Inc., Turkey | 13.50 | 20.20 | 35.04 | 4.00 | 5.30 | 0.33 | 0.39 | 9.40 | 8.44 | – | [55] |
| ALCOA factory, San Cibrao (Northwest of Spain) | 9.00 | 12.00 | 37.00 | 20.00 | 6.00 | – | – | 5.00 | – | – | [52] |
| Korea Chemical Co. | 22.90 | 23.70 | 16.60 | 6.70 | 6.70 | – | – | 11.60 | – | – | [56] |
| Shandong Aluminium Factory, China | 21.90 | 7.96 | 6.57 | – | 38.84 | 1.60 | 0.41 | 2.32 | 17.42 | – | [57] |
| Greek red mud, Greece | 9.20 | 15.60 | 42.50 | 5.90 | 19.70 | – | – | 2.40 | – | – | [58] |

Table 2
Surface area increase in red mud following treatments

| S. no. | Surface area before treatment (m$^2$/g) | Surface area after treatment (m$^2$/g) | Surface area increase (%) | Treatment | References |
|---|---|---|---|---|---|
| 1 | 64.0 | 155.0 | 1.42 | ARM[a] | [71] |
| 2 | 25.5 | 184.1 | 6.21 | ARM[a] | [72] |
| 3 | 29.4 | 60.7 | 1.06 | ARM[a] | [73] |
| 4 | 24.3 | 82.4 | 2.39 | ARM[a] | [75] |
| 5 | 24.3 | 85.4 | 2.51 | SARM[c] | [75] |
| 6 | 24.3 | 29.5 | 0.21 | SRM[c] | [75] |
| 7 | 28.3 | 131.1 | 3.63 | ARM[a] | [86] |
| 8 | 28.3 | 111.7 | 2.94 | PARM[b] | [86] |

[a] ARM-HCl activated red mud.
[b] PARM-HCl + H$_3$PO$_4$ activated red mud.
[c] SRM-Sulphided red mud.

catalytic activity easily [78]. The effectiveness of such catalysts, however, has been low mainly because of their low surface area and low level of dispersion i.e. number of catalyst particles per unit reacting volume [79]. The activity of these 'alternate sources' of the catalyst can be increased by certain treatments like sulphidation and size reduction [80]. In addition they do not need to be recovered after the reaction, unlike the other expensive catalysts [81].

Mitra et al. [82] suggested that hydrated iron oxide deposited on coal might be considered as an "improved substitute" for such materials like red mud and iron ore. A comparative study was conducted between two different modes of iron oxide catalyst for coal hydrogenation. First mode consisted of hydrated iron oxide deposited on coal (200 mesh) by means of precipitating it in an aqueous iron salt solution. In the second mode the precipitated hydrated iron oxide was mechanically mixed with the powdered coal (200 mesh). The prepared coal mass consisted of 2.52% Fe on dry weight basis. The experiments were conducted using two types of pasting media (tetralin and tar oil) having different hydrogen donating properties. The reaction conditions used were 24.5 MPa H$_2$ pressure, 450 °C temperature and 90 min experimental time. Calculations of the conversion of coal to gas and liquid were done on the basis of benzene solubility. The best results under the given reaction conditions, in terms of conversion were
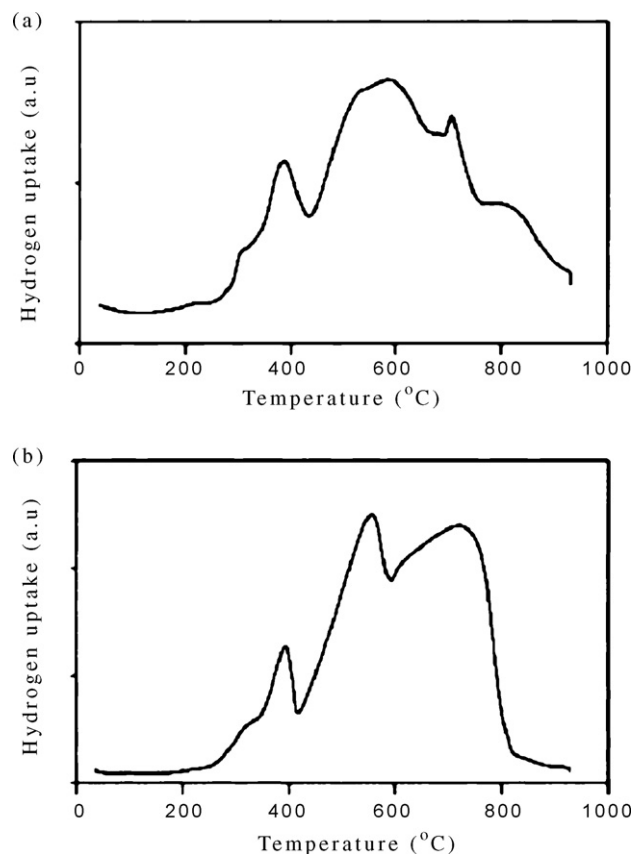


Fig. 1. TPR profile of (a) red mud and (b) α-Fe$_2$O$_3$ (reprinted from [62], with permission from Elsevier).

~95%. This was attained at around 30 min and remained stable thereafter. The results were found to be similar for both the deposited and mixed catalyst. However, in terms of overall activity and selectivity (considering asphaltene yield, gas yield and product quality), the deposited catalyst was found to be superior.

Mastral et al. [67] compared the different modes of addition of iron catalysts for the hydrogenation of high sulphur-low rank coals. They used three kinds of iron catalyst precursors namely red mud, iron(II) sulphate heptahydrate and iron pentacarbonyl. In all cases the final catalyst loading was 5% Fe by dry ash free weight of coal. The coals to be tested were ground and sieved to

Table 3
Conversion efficiencies for various reactions employing red mud as catalyst

| Application | Catalyst | Temperature °C (pressure) | Conversion% | References |
|---|---|---|---|---|
| Organochlorinated compounds hydrodechlorination | Calcined red mud | 300 | 39 | [50] |
| Coal hydrogenation | Untreated red mud | 400 (10 MPa H$_2$) | >90 | [67] |
| Coal liquefaction | Sulphur promoted red mud | 450 | 7.2 mol | [68] |
| Rye straw hydrogenation | Untreated red mud | 400 | 99 | [69] |
| Biomass liquefaction | Sulphur promoted red mud | 400 | 99 | [69] |
| Naphthalene hydrogenation | Activated red mud | 350 (3.45 MPa) | 49 | [71] |
| Naphthalene hydrogenation | Activated red mud | 405 (6 MPa) | 80 | [72] |
| Methane combustion | Activated red mud | 650 | ~100 | [86] |
| SO$_2$ reduction | Untreated red mud | 640 | 30 | [87] |
| Nitric oxide oxidation | Cu impregnated red mud | 350 | 50 | [89] |

60 mesh. Red mud was mixed manually to the ground sieved coal; iron(II) sulphate heptahydrate was added in the form of precipitate to the aqueous coal slurry while iron pentacarbonyl was directly imbedded onto the coal under inert atmosphere. The reaction was conducted at 10 MPa $H_2$, 300–450 °C temperature and 30 min reaction time. Four different sub-bituminous coals were used for the analysis.

The presence of $H_2S$ in the initial stages of the hydrogenation reaction was found to suppress the regressive reactions that lead to the formation of products other than the desired liquid release. In sub-bituminous coals with high sulphur content, hydrodesulphurization takes place during the hydrogenation reaction producing $H_2S$. Therefore, the addition of any external source of sulphur is not required. Hydrogen sulphide, produced by the reduction of organic sulphur and/or pyrite improved the conversion efficiency by causing the sulphidation of the transition metals. It also helped in breaking the bond present in coal macromolecular structure. Different conversion yield (in terms of oil, asphaltenes and gas) were observed at different temperatures. The results further indicated that under certain conditions red mud gave the best results (>90% at 400 °C), despite poor dispersion. This divergence was due to the fact that the temperature at which red mud becomes active (400 °C), the catalyst dispersion was not very relevant as the portions of coal were already in liquid form. In comparison, the other catalyst precursors like iron(II) sulphate heptahydrate and iron pentacarbonyl did not present any better results than the manually added red mud.

Hydroliquefaction of coal was also investigated by Yokoyama et al. [68] with sulphur promoted red mud and other iron containing catalysts ($FeS_2$, $Fe_2O_3/S$, $Fe_3O_4/S$ and $FeSO_4$) using diphenylether (DPE) and diphenylmethane (DPM) as model compounds. The effect of formation of sulphate on the reaction was also studied. Sulphate was formed in each case by the reaction between water and the sulphur promoted catalysts. Analytical results obtained for sulphate for all catalysts in presence of diphenylmethane was larger than for diphenylether. This was because of the stronger affinity between water and diphenylether than water and diphenyl-methane. In case of sulphur promoted red mud the sulphate wt% for diphenylmethane was 6.6 as compared to 2.4 for diphenylether. The mol% conversion achieved on hydrotreatment of diphenylmethane in case of sulphur promoted red mud in absence and presence of water was 6.8 and 3.6, respectively. This was similar to the results obtained for $FeS_2/H_2O$ (7.2 mol%) and sulphur promoted $Fe_2O_3$ (7.1 mol%) but lower than that obtained for $FeS_2$ (23.4 mol%). The lower value with water was primarily due to the formation of sulphate on the surface of the catalyst. Out of the hydrocracked products of diphenylmethane (benzene, toluene, bibenzyl, anthracene, triphenyl methane and other unknown products) the selectivity of benzene (36.6%) was higher in case of sulphur promoted red mud in absence of water. For toluene (36.4%) and bibenzyl (56.1%) it was higher for sulphur promoted red mud in the presence of water. The results obtained for hydrotreatment of diphenylether were 9.6 and 2.4 (mol%) for sulphur promoted red mud in absence and presence of water, respectively. Sulphur

promoted red mud in absence of water had the highest mol% conversion followed by $FeS_2$ and $Fe_2O_3$ (sulphur promoted). The percent selectivity for benzene (54.6%, 54.9%) and phenol (45.4%, 45.1%) was comparable and relatively high for sulphur promoted red mud both in absence and presence of water.

Klopries et al. [69] conducted hydrogenation experiment to study the catalytic property of red mud for the hydroliquefaction of rye straw using tertalin and compared it to other commonly used hydrogenation catalyst $CoO-MoO_3/Al_2O_3$. It was found that red mud was able to catalyze the liquefaction of biomass in the presence of sulphur, but was inferior to the activity of $CoO-MoO_3$ catalyst. Red mud not only required sulphur as catalyst but also demanded higher temperatures (400 °C) for the reaction to take place. Matching results were achieved by $CoO-MoO_3$ catalyst at the same temperature without the need for any sulphur addition; however on addition of sulphur the reaction took place at a lower temperature of 350 °C. Addition of sulphur plays a role in hydrodeoxygenation and also decreases the coking tendency of the catalysts thereby increasing the hydroliquefaction potential. During the reaction hydrodeoxygenation and hydrocracking reactions take place on the products of pyrolysis, yielding $C_1$–$C_4$ hydrocarbons, gasoline and heavy oils. With an increase in temperature the quantity of $C_1$–$C_4$ hydrocarbons showed an increase mainly due to the enhanced hydrocracking reactions.

The experiment performed in absence of the catalyst to evaluate the hydrogenation activity revealed that approximately 90% of liquefaction could be achieved; the addition of red mud and sulphur further hydrogenated the remaining 10% coal like substance to oil, phenols and gasoline, increasing this percentage to ∼99% at 400 °C. $CoO-MoO_3/Al_2O_3$ demonstrated higher conversion percentage of 99.5%.

In a more recent study, high surface area (100–250 $m^2$/g) iron oxide based catalysts, were prepared in the presence of an anion such as molybdate, phosphate, sulfate or tungsten. These were promoted by the addition of an active hydrogenation stabilization metal like cobalt, molybdenum, tungsten or their combinations. The catalysts were found to have high catalytic activity for hydrogenation and hydroconversion of carbonaceous material like coal, heavy petroleum, waste plastic etc. into low boiling hydrocarbon liquid and gaseous products [79]. However, in comparison to pure iron oxide, red mud is considered a better hydrogenation catalyst mainly due to its titanium oxide impurity [78].

Pratt and Christoverson [71] used red mud as a primary catalyst for hydrogenation of multi-ring aromatics such as naphthalene to tetralin. The activity of red mud was investigated after simple activation process with HCl. It was found that the conversion percentage for naphthalene to tetralin for untreated 'as received' red mud with a surface area of 64 $m^2$/g was 3.55% and for calcined red mud (500 °C for 2 h) the percentage was 3.85%. After activation of red mud by acid dissolution and precipitation the surface area increased to 155 $m^2$/g and the conversion efficiency to 49%. Further addition of 20% $TiO_2$ increased the conversion percentage to 58%. The increase in activity after acid activation was attributed to a 150% increase in surface area along with the
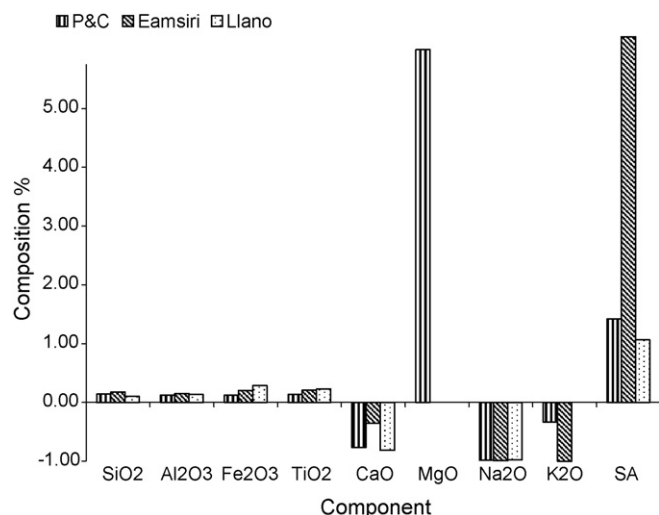
Fig. 2. Percentage difference in component percentage in pre and post activation red mud (P&C: Pratt and Christoverson [71]; Eam: Eamsiri et al. [72]; Llano et al. [73]; SA: surface area).

removal of Ca and Na. An overall increase in the intrinsic catalytic activity of the material was observed. In untreated and treated red mud, the wt% of CaO and $Na_2O$ decreased from 3.84 and 6.03 to 0.90 and 0.12, respectively. The percentage difference in the pre and post activation composition of red mud is given in Fig. 2; comparison with other studies shows a similar trend in composition change with activation. Testing of synthetic red mud revealed Na and Ti to have the most significant effect on the intrinsic catalytic activity apart from iron, which is the true catalyst here (Fig. 3). Although Na contributes to the catalytic activity, it decreases the surface area, since it is a sintering agent for $Al_2O_3$. Presence of Ti, however, demonstrates a positive effect on the catalytic activity. The exact role of Na and Ti was not mentioned, however the

possible reason for the increase in activity by the addition of $TiO_2$ was attributed to the activation of hydrogen by $TiO_2$.

Red mud activated by the method described by Pratt and Christoverson was examined for the hydrogenation of highly condensed aromatics and for the hydroliquefaction of high and low rank coals. The activity of the catalyst for the hydrogenation of naphthalene, phenanthrene and pyrene was compared with a commercial catalyst of nickel molybdate with a surface area 160 $m^2/g$, containing 3%, NiO, 15% $MoO_3$ on γ-alumina. Conversions obtained for hydrogenation reaction were best for nickel molybdate followed by activated red mud. Untreated red mud showed poor results [72].

The reactions conducted under similar conditions i.e. 3.45 MPa pressure and 350 °C for 5 h, in the two studies by Eamsiri et al. [72] and Pratt and Christoverson [71] for hydrogenation of naphthalene show comparable results of conversion efficiency for activated red mud (47% and 49%, respectively). The conversion of naphthalene over activated red mud at 6 MPa pressure and 405 °C for 1 h, showed enhanced conversion efficiency (80%) [72]. The same was not observed for the other two aromatic compounds indicating that the effect of temperature and pressure on conversion efficiency was greater for naphthalene. The superior efficiency of activated red mud over untreated red mud was attributed to the increase of surface area of the former from 25.5 to 184.1 $m^2/g$ and the simultaneous reduction in $Na_2O$ content from 9.8 to 0.1%.

The hydroliquefaction reactions of coal were performed using red mud, activated red mud and pre-sulphided nickel molybdate catalyst. The reaction conditions used were 6 MPa initial hydrogen pressure, 405 °C temperature and 1 h reaction time. The tests were done using two different types of coal, that were slurried in 1:1 ratio with tetralin (hydrogen donar solvent). The catalyst concentration was 300 mmol of Fe $kg^{-1}$ dry coal (300 mmol of Mo $kg^{-1}$ dry coal in case of nickel molybdate
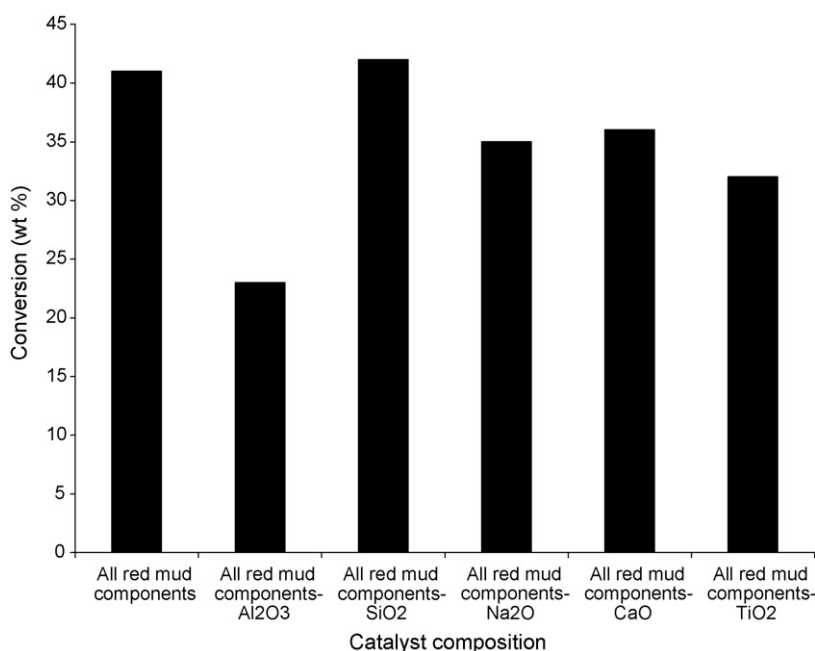


Fig. 3. Conversion of naphthalene to tetralin vs. composition of synthetic red mud [71].

catalyst) and carbon disulphide was the sulphur source. It was found that activated red mud was only slightly better than red mud, and both were inferior to the nickel molybdate catalyst. The best conversion obtained for red mud and activated red mud with tetralin as solvent was 72% and 75%, respectively. In the absence of any catalyst 64% conversion was achieved. On adding small quantities of tin, a minor increase was observed in the conversion for both red mud (79%) and activated red mud (77%). However, this increase was observed only in the presence of $CS_2$ [72].

Llano et al. [73] tested red mud as a hydrogenation catalyst for anthracene oil, a fraction obtained from coal tar distillation. Upon hydrogenation the condensed aromatic hydrocarbons present in the oil get transformed to hydroaromatics, which produce hydrogenated solvent with hydrogen donor capacity. In the previous studies [71,72], the hydrogenation potential of the catalyst was tested for pure polycyclic aromatic hydrocarbon compounds only; however in this study complex polycyclic aromatic hydrocarbon fractions (anthracene oil) from the industry were tested. Anthracene oil primarily consists of phenanthrene, anthracene and carbazole. Red mud, activated red mud and Ni-Mo/γ-alumina commercial catalyst were tested and compared for their hydrogenation potential. During the experiments the catalysts were maintained in sulfided form. The tests were carried out at 350 °C, 10 MPa and $H_2$ flow rate of 4 ml/s at standard temperature and pressure.

Initial composition of anthracene before the hydrogenation identified the major components as 9,10-dihydroanthracene, fluoranthene, pyrene, fluorene, anthracene etc. Napthalene, acenapthalene, anthracene, phenanthrene, fluoranthene and pyrene were found to be hydrogenated to a considerable degree. In terms of total conversion of all compounds, the commercial catalyst (surface area: 243 m²/g) was found to be more active than red mud (surface area: 29.4 m²/g) and activated red mud (surface area: 60.7 m²/g), however in terms of more specific hydroaromatic concentration, activated red mud showed better results. It was also found that except for naphthalene, activation treatment enhanced the hydrogenation activity. In contrast, the previous studies [71,72] that tested the hydrogenation potential of naphthalene in pure form by red mud and activated red mud had shown an increase in the catalytic activity following activation. This indicates that the activity of the catalyst differs for pure and complex compounds. Also in those studies, the surface area of activated red mud was higher.

Studies were also conducted on the characterization and deactivation of red mud as hydrogenation catalyst for anthracene oil under similar conditions as described by Llano et al. [74,75]. As in the case of Llano et al., the constituents of anthracene that were hydrogenated to considerable degree were anthracene, phenanthrene, fluoranthene and pyrene. The main cause of deactivation of red mud during the reaction was attributed to the loss of surface area and surface iron content. As the reaction proceeded, in addition to iron, the content of titanium, calcium, silicon and sodium were found to decrease as well, and at a faster rate than iron. Chlorine, sulfur and aluminium content were found to increase (Table 4). The loss of activity was more pronounced in the case of non activated

Table 4
Composition (wt%) of sulphided (activated and non-activated) red mud after 12 h reaction time [74,75]

| Element | Non activated sulphided red mud | | Activated sulphided red mud | |
|---|---|---|---|---|
| | Initial | After 12 h reaction time | Initial | After 12 h reaction time |
| Fe | 36.7 | 35.8 | 41.0 | 34.4 |
| Al | 11.3 | 14.9 | 14.9 | 21.0 |
| Cl | 1.0 | 3.7 | 0 | 0.7 |
| Ti | 17.9 | 13.4 | 15.2 | 16.1 |
| Ca | 7.6 | 5.1 | 4.0 | 5.3 |
| Si | 6.2 | 4.1 | 3.9 | 2.9 |
| Na | 4.0 | 2.4 | 4.0 | 5.3 |
| S | 14.5 | 19.4 | 19.8 | 17.1 |
| Surface area (m²/g) | 29.5 | 18.3 | 85.4 | 49.3 |

sulfided red mud (surface area: 29.5 m²/g) than activated sulfided red mud (surface area: 85.4 m²/g), which shows that activated sulfided red mud is a better hydrogenation catalyst for anthracene oil.

Iron oxide was studied for the selective hydrogenation of acetic acid to acetaldehyde over pure untreated α-$Fe_2O_3$ catalyst and a prepared α-$Fe_2O_3$ catalyst [83]. Both the catalyst behaved in similar manner; however, the pre-reduced form of the latter was found to be less resistant to reaction temperatures above 400 °C. This indicated that the preparation method of the catalyst affected its properties. The reaction products were acetone, acetaldehyde, water, $CO_2$ and CO and the temperature at which the reaction started was 340 °C. It was found that the selectivity to acetaldehyde increased in the case of pre-reduced catalyst. This was primarily due to the conversion of a part of the $Fe_2O_3$ catalyst to metallic Fe, which helped in activating the hydrogen. The actual hydrogenation reaction takes place on the oxide phase via Mars and Van Krevelan mechanism. A high hydrogen/acid ratio is essential for the reaction to take place smoothly.

Hydrocracking, a two stage process combining catalytic cracking and hydrogenation has been tried using industrial wastes like red mud, copper industry waste, steel making waste etc. as catalyst in the form of slurry bed reactors. Use of such wastes as catalyst helps offset the operation costs. There are various slurry bed hydrocracking processes in different stages of development. Some of the known processes include HDH (Hydrocracking Distillation Hydrotreating) process developed by Venezuelan Intevep and German VCC (Veba Combi Cracking) process [76].

### 3.2. Red mud catalyst in hydrodechlorination reactions

Hydrodechlorination (HDC) reactions involve the reaction between hydrogen and organic molecule containing C–Cl bond, to form HCl and C–H bond.

$$R-Cl + H_2 \rightarrow R-H + HCl$$
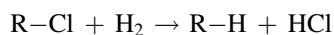
Red mud has been studied as a catalyst for tetrachloroethylene hydrodechlorination [61,62] and catalytic detoxification of $C_2$-chlorohydrocarbons [50].

Various organochlorinated compounds are used widely as pesticides, solvents, degreasing agents, extractants etc. However, they are highly toxic and do not degrade easily, thus, posing a threat to the environment [84]. One of the common methods used for their abatement is thermal incineration. However, there are many disadvantages attached to it, such as release of harmful partial oxidation products like phosgene, dibenzofurans, dibenzodioxins etc., and high temperatures for combustion due to the presence of high amount of chlorine. In comparison to thermal incineration, catalytic hydrodechlorination has several advantages as it takes place at much lower temperature, produces less harmful reaction products and can be disposed off comparatively easily. Some commonly used catalysts are precious metals like platinum (Pt), palladium (Pd) and rhodium (Rd) and certain other hydro-treatment catalyst like Ni-Mo [21]. However, the problems associated with its use are the high cost and its susceptibility to getting poisoned by HCl and other organosulphur/organonitrogen compounds produced in the reaction. Studies have shown that hydrodechlorination can also be catalyzed by transition metal sulfides of V, Cr, Mn, Fe, Co, Ni, Mo, Ru, Rh, Pd, W, Ir and Pt. However, these are also susceptible to chlorine poisoning.

Ordóñez et al. [61] studied the catalytic hydrodechlorination of tertachloroethylene (TTCE) over red mud. It was found that sulfided red mud was an active hydrodechlorination catalyst due to its iron sulfide content. The tests were conducted in continuous fixed bed reactor made of stainless steel. The influence of catalytic sulphiding, temperature, pressure, hydrogen flow rate and presence of different solvents like benzene, toluene, hexane and heptane were analyzed. It was concluded that catalytic sulphiding, increase in temperature and pressure had a positive influence on the catalytic activity of red mud, while the presence of solvent did not have an effect. Similar results were obtained by Martino et al. [85] for the hydrodechlorination of dichloromethane, tricholroethane, trichloroethylene and tetrachloroethylene over sulfided Ni/Mo-γ-alumina catalyst.

In the deactivation study of sulfided red mud conducted by Ordonez et al. [62] it was postulated that the main cause of deactivation could be the conversion of Fe, initially present in the pyrrhotite form to iron(II) sulphide. This conversion could also be seen by the XRD patterns of the samples obtained (Table 5). It was suggested that this conversion might have taken place due to the presence of certain compounds produced during the reaction. The nitrogen adsorption studies conducted, revealed that the phenomena causing the loss of surface area were not the primary contributor to the deactivation.

Table 5
Comparison of the mineralogical composition of sulphided red mud at different times of experimental run [62]

| Time | Mineral composition |
| --- | --- |
| Fresh | Rutile, pyrrhotite, bayerite, hematite |
| Post 2 h | Rutile, pyrrhotite, halloysite, iron sulphide |
| Post 4 h | Rutile, pyrrhotite, halloysite, iron sulphide |
| Post 12 h | Rutile, pyrrhotite, halloysite, iron sulphide |
| Post 60 h | Rutile, iron sulphide, halloysite, hematite, |

Dechlorination of five organochlorinated compounds (1,2-dichloroethane (DCE), 1,1,2-trichloroethane (TRCE), 1,1,2,2-tetrachloroethane (TCE), trichloroethene (TRCEE) and 1,1,2,2-tetrachloroethene (TCEE), was catalyzed over pretreated red mud by Halász et al. [50]. They compared it with other catalyst like crystalline and amorphous $Fe_2O_3$ (surface area: 4.5 $m^2$/g and 55 $m^2$/g), $Fe_2O_3/Al_2O_3$ (surface area: 103 $m^2$/g) and Fe-ZSM5 (surface area: 335 $m^2$/g), a modified zeolite catalyst. The zeolite catalyst had the highest surface area and also the best conversion percentage (55% at 300 °C). However, owing to deactivation by HCl, it had a small lifetime. At the same temperature red mud calcined at 500 °C for 4 h was able to give a conversion percentage of 39%, which was superior to the other tested catalysts. It demonstrated good catalytic activity in the oxidative removal of halogenated hydrocarbons as well as in the reduction of light chlorohydrocarbons. Moreover the reactions taking place over red mud caused a decrease in alkalinity of red mud making it more apposite for disposal.

### 3.3. Red mud as exhaust gas clean-up catalyst

For the destruction of certain air emissions, red mud has been studied in the catalytic combustion of methane [86], recovery of sulphur from sulphurous waste gases [87], elimination of volatile organic compounds [88], selective catalytic reduction of nitric oxide [89,90], treatment of exhaust gases for HCl, carbon monoxide and dioxins [91], hot gas clean up of coke oven gases and gasification products [49].

Catalytic combustion of methane is an attractive option for reducing the methane emissions in the atmosphere. It is desirable that the catalyst be stable at high temperature and resistant to sintering. In addition, it must be active even at low temperatures and be cost effective. Noble metals like palladium (Pd) and iridium (Ir) are considered one of the most effective catalysts for methane combustion [86]. However, their use is limited due to high cost, susceptibility to poisoning, sintering and volatilization at high temperatures [92].

Paredes et al. [86] prepared three iron based catalysts using red mud for the catalytic combustion of methane, and to study the activity and stability of the catalysts. Iron oxide (hematite) (surface area: 6.6 $m^2$/g) and Cu-Cr-Ti, a commercial catalyst (surface area: 52.7 $m^2$/g) were used as reference material for comparing the efficiency of the prepared catalysts. The three catalysts tested consisted of red mud (surface area: 28.3 $m^2$/g), red mud activated by the Pratt and Christoverson [71] method (surface area: 131.1 $m^2$/g), and red mud treated by the Alvarez [74] method (surface area: 111.6 $m^2$/g). The Alvarez method consisted of dissolving red mud in a mixture of ortho-phosphoric acid and hydrochloric acid, followed by precipitation and calcination. The results indicated that red mud showed the least activity, while activated red mud showed the best potential for the catalytic combustion of methane both in terms of activity and deactivation resistance. The performance of activated red mud was also at par with that of pure hematite and better than the commercial catalyst (Fig. 4). The loss of surface area (after 110 h of reaction the surface area decreased from
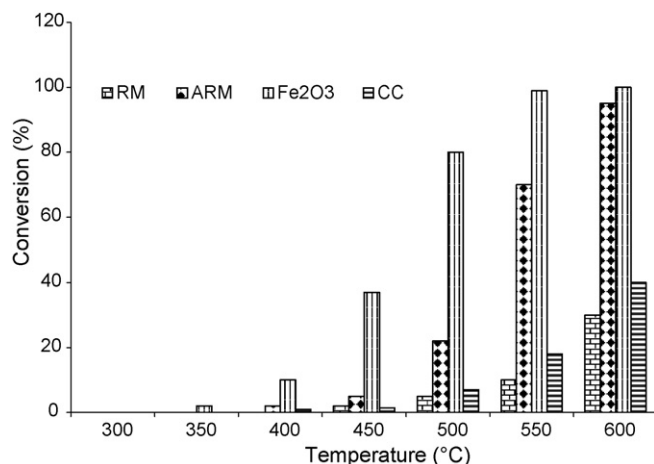
Fig. 4. Combustion of methane (2000 ppmV) over red mud (RM), activated red mud (ARM), ferric oxide (Fe$_2$O$_3$) and commercial catalyst (CC) [86].



Fig. 5. Loss of surface area of activated red mud with time [86].

131.1 to 88.6 m$^2$/g) was the main cause of deactivation of activated red mud. The poor activity of red mud was attributed to the presence of certain other constituents for e.g. Ti as rutile and Al as gibbsite and goethite, which are catalytically inert. TiO$_2$ in the anatase form has been found to be catalytically superior to rutile phase in a study on photodegradation [93].

Presence of Na and Ca also contributed to the poor activity of red mud as they promote sintering, thus decreasing the surface area. In case of acid treated red mud Na and Ca content is decreased and the surface area increases. However, compared to activated red mud, phosphorous-activated red mud shows slightly lower activity as higher amounts of phosphorous lead to a decrease in the surface area. The Temperature Programmed Desorption (TPD) experiments conducted on the activated red mud, phosphorous-activated red mud and ferric oxide suggested the amount of methane adsorbed on the catalyst was quite low. The reticular oxygen of the catalyst was adequate for the complete oxidation of methane.

Two types of tests were conducted for studying the stability of the catalysts. The first experiment included recording the methane concentration while successively increasing the temperatures from 300 to 626 °C and decreasing from 626 to 300 °C. The results revealed that pure iron oxide was more resistant to deactivation than both activated red mud and phosphorous-activated red mud. Second experiment was carried out at a constant temperature (625 °C) and its results demonstrated that red mud and phosphorous-activated red mud were deactivated more quickly than pure hematite and activated red mud. Contrary to the well known promoting effect of phosphorous on the stability and activity of catalysts in hydrogenation reactions, its addition in this case, did not contribute to improving the activity. The main cause of the deactivation of activated red mud was attributed to the loss of surface area (Fig. 5). It was observed that despite having a very low surface area, the iron oxides gave better results in terms of activity per unit surface area than the red mud catalysts. Red mud demanded much higher temperature for obtaining similar moles of methane converted per minute per meter square of surface area in comparison to iron oxide catalyst. This was
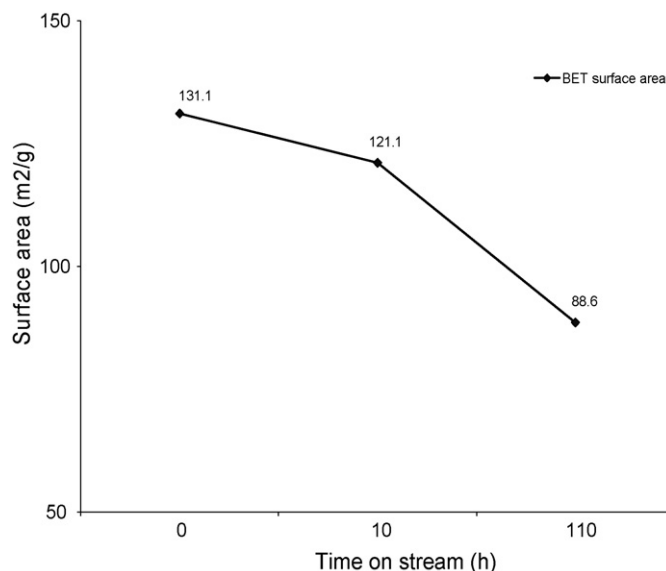
primarily due to the fact that iron oxide was completely formed of hematite, the main component taking part in the reaction, as against the mixed composition of red mud derived catalysts.
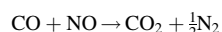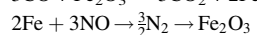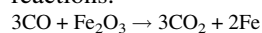
In methane combustion over unsupported iron oxide catalyst carried out by Barbosa et al. [65] it was found that calcination temperature used for the preparation of the catalyst was an important factor in determining the catalytic property of the catalyst. The preparation method employed for the iron oxide also influenced the surface area, stability and activity of the catalyst. Iron oxide prepared by precipitation method, calcined at 600 °C and having a surface area of 18.5 m$^2$/g, showed a methane conversion percentage approaching 100 at ∼650 °C. These results are similar to the results obtained by Paredes et al. [86] for activated red mud. For the other iron oxide catalysts prepared by both citrate and precipitation method, calcined at different temperatures, higher temperatures were required to achieve similar conversion percentage. As in the case of Paredes et al. [86] sintering was the main cause of deactivation. On comparison of the two studies [65,86] it can be seen that the iron oxide prepared by precipitation method and calcined at 600 °C, after 110 h on stream, retained ∼80% of its initial activity, in comparison to 70% retained by activated red mud. The decrease in surface area for the iron oxide catalyst was 28% in the initial 60 h of reaction with a corresponding 15% decrease in activity. It was found that sintering was influenced by the operating and calcination temperature. Sintering was higher if the operating temperature exceeded the calcination temperature.

Lamonier et al. [89] studied red mud and red mud impregnated with Cu for the selective catalytic reduction of nitric oxide. The tests were conducted both in the presence and absence of O$_2$. Prior to the tests, the solids were either dried under a flux of helium or reduced with hydrogen. In addition, the selectivity of N$_2$O, a possible product of NO reduction, was also studied as a function of temperature. The reducing agent used for the experiment was ammonia because of its selective

nature towards NO even in the presence of $O_2$. The reaction between NO and $NH_3$ on metal oxide catalyst is as follows:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$
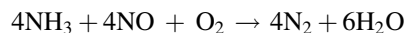
The results obtained for the conversion of NO over red mud dried at 500 °C and red mud reduced under $H_2$ at 500 °C revealed that in the latter case the conversion of NO begins at a lower temperature, 100 °C, as compared to ~250 °C in the former. This has been attributed to the possible reduction of ferric oxide leading to a more active catalyst. Similar results were obtained by Hayhurst and Lawrence [94], for the reduction of NO and $N_2O$ to $N_2$ in the presence of iron and its oxides by CO. It was found that the metallic iron was far superior to its oxides in decomposition of NO and $N_2O$. NO reduction by CO over $Fe_2O_3$ takes place via the following reactions:

$$3CO + Fe_2O_3 \rightarrow 3CO_2 + 2Fe$$
$$2Fe + 3NO \rightarrow \tfrac{3}{2}N_2 \rightarrow Fe_2O_3$$

$$CO + NO \rightarrow CO_2 + \tfrac{1}{2}N_2$$

The chemical reaction between $N_2O$ and CO takes place via the process:

$$N_2O + CO \rightarrow N_2 + CO_2$$
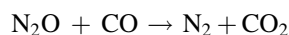
In general the presence of $O_2$ in small percentage is known to accelerate the NO conversion. Studies conducted by Bauerle et al. [95], Inomata et al. [96] and Djerad et al. [97], show that in presence of small amount of oxygen, the rate of reduction of NO by $NH_3$ increases noticeably. This increase is primarily due to the conversion of part of NO to $NO_2$ in the presence of oxygen. Studies of Inomata et al. [96] showed that the rate of NO conversion over $V_2O_5$ catalyst increased from 10% in absence of oxygen to 50% in presence of oxygen at 250 °C. However, in the present case no beneficial effect of the presence of $O_2$ was observed on the reaction. Moreover the presence of 2% $O_2$ in the reaction mixture diminished the activity of dried red mud (Fig. 6). The initial temperature required for the conversion to start increased from 100 °C in the absence of oxygen to 230 °C in the presence of oxygen. This deviation was attributed to the adsorption of $O_2$ on the active sites of red mud
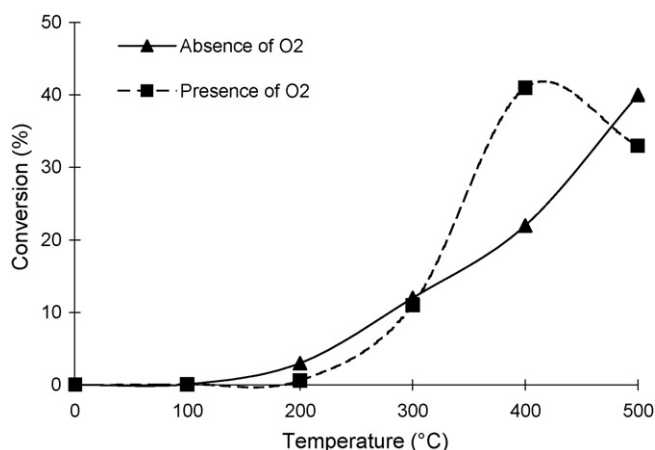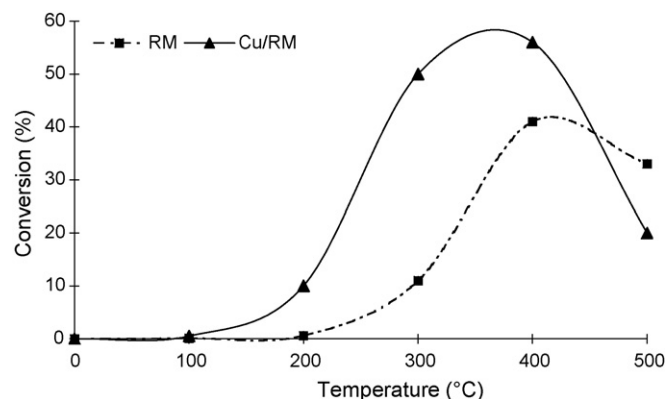


Fig. 7. NO reduction over red mud and Cu/red mud in presence of $O_2$ [89].

that played an inhibiting role. Nevertheless the rate of increase of activity with temperature was higher with the addition of 2% $O_2$ to the reaction mixture. A 40% conversion of NO was achieved at 400 °C in presence of $O_2$ as against 540 °C in its absence. The selectivity of $N_2O$ was greater in the absence of $O_2$ and grew rapidly from 30 to 40% at a temperature of 250 °C to 80% at 500 °C. An initial reducing treatment of red mud under $H_2$ at 500 °C improved the selectivity of $N_2O$ but the catalytic activity of the reduced red mud diminished. In fact at 400 °C only 25% of NO was converted using reduced red mud while with dried red mud 40% NO was converted. In the second part of the experiment the red mud was impregnated with 5% Cu which noticeably improved the catalytic performance of red mud. At 250 °C, 30% of NO was converted as against 10% in first test (Fig. 7). Also in contrast to dried red mud, in case of Cu impregnated red mud, presence of $O_2$ improved both, the activity and selectivity.

On comparison between certain other catalysts like Cu impregnated zeolites and $Cu/Al_2O_3$, it was found that in presence of oxygen, industrial catalyst Cu/zeolite had the best performance. At 150 °C, the conversion of NO reached 70%. At higher temperature (~350 °C) it was able to achieve 100% conversion. It also did not favor the parasitic oxidation of $NH_3$ by $O_2$ at high temperatures. The catalytic activity of $Cu/Al_2O_3$ (90%) was also found to be superior to that of Cu/red mud (50%). Nonetheless both had the same selectivity for $N_2O$ [89].
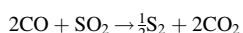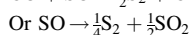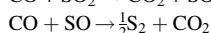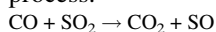
Apostolescu et al. [98] studied $Fe_2O_3$ based materials for the selective catalytic oxidation of $NO_x$ in diesel exhaust, using ammonia. Several carriers were screened to estimate the most effective support for the catalyst. The effect of tungsten oxide over the catalytic activity was also investigated. The results revealed that out of $MgAl_2O_4$, $ZrO_2$, $SiO_2$ and $TiO_2$, $ZrO_2$ was the most effective carrier for $Fe_2O_3$. The best activity was obtained for 1.4 mol% $Fe_2O_3$ and 7.0 mol% $WO_3$ on $ZrO_2$ carrier; this gave complete conversion at a temperature of 285 °C. In comparison, pure $\alpha$-$Fe_2O_3$ gave a conversion of only 43% at 255 °C.

Red mud has also been studied as a catalyst for reduction of $SO_2$ using CO. The materials examined were red mud from two sources, two types of zeolites, red bauxite, buechler alumina and iron alumina (Table 6). It was found that the materials having high $Al_2O_3$ and Fe content exhibited good catalytic



Fig. 6. Reduction of NO over red mud in presence and absence of $O_2$ [89].

Table 6
Details of catalysts used for $SO_2$ reduction [87]

| Material | Surface area ($m^2$/g) | $Al_2O_3$ (%) | Total Fe (%) |
|---|---|---|---|
| Red bauxite | 100.4 | 53.1 | 6.6 |
| Surinam red mud | 7.91 | 20.7 | 15.7 |
| Jamaican red mud | 12.23 | 23 | 27.4 |
| Zeolite | 5.9 | 39.1 | 0.4 |
| Buehler alumina | 7.4 | 99.+ | – |

activity. This is attributed to the 'dual site mechanism' wherein $SO_2$ gets preferentially chemisorbed on alumina while CO is chemisorbed on iron. The reaction takes place via the following process:

$$CO + SO_2 \rightarrow CO_2 + SO$$
$$CO + SO \rightarrow \tfrac{1}{2}S_2 + CO_2$$
$$Or \ SO \rightarrow \tfrac{1}{4}S_2 + \tfrac{1}{2}SO_2$$

$$2CO + SO_2 \rightarrow \tfrac{1}{2}S_2 + 2CO_2$$

Red bauxite and Surinam red mud exhibited the highest catalytic activity ($\sim$30% at around 640 °C) for the CO–$SO_2$ reaction. Jamaican red mud also showed good activity ($\sim$26% around 500 °C). However, other materials having very low or negligible iron showed poor activity [87].

Hot gas clean up of coke oven gases and gasification products was achieved by using a sorbent made by palletizing red mud particles. The reducing components were in significant excess compared with $H_2S$. The clean up takes place via the following reaction [49]:

$$Fe_2O_3 + CO/H_2 \rightarrow 2FeO + CO_2/H_2O$$

$$FeO + H_2S \rightarrow FeS + H_2O$$
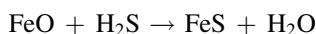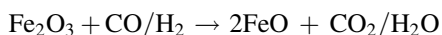
Furimsky and Biagini [99] described the potential of using spent decoked hydroprocessing catalyst as hot gas cleanup sorbents. In the study it was found that the catalysts deposited by coke demonstrated good gas cleaning efficiency. Another study used spent decoked catalyst for decomposition of $H_2S$ instead of fresh catalysts; it was revealed that the decomposition was more than 80% in case of the former as compared to the latter. This activity could further be increased by doping of Mo species in case of direct $H_2S$ decomposition [100].

### 3.4. Red mud as catalyst in miscellaneous reactions

Red mud has also been studied in other reactions like degradation of poly (vinyl chloride) containing polymer mixture into fuel oil [53,101], conversion of waste oil and waste plastic to fuel [102], heavy crude oil hydrotreating [103], hydrodemetallization of hydrocarbons containing metallic compounds as impurities and hydro-treating such hydrocarbons [104], ammonia decomposition in presence of sulphur compounds [105], nitrile synthesis from aldehydes and hydroxyamine [106].
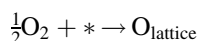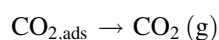
Metal impregnated red mud has been studied for wet oxidation of organic substances [107], thermal catalytic hydroconversion process (as first stage catalyst in a two stage process) [108].

Yanik et al. [53] investigated the catalytic properties of red mud for degradation of poly (vinyl chloride) containing polymer mixture (poly vinyl chloride/high density polyethylene, poly vinyl chloride/poly propylene and poly vinyl chloride/poly styrene) into fuel oil. Both thermal and catalytic degradations were tested in the study. Red mud was used as a cracking catalyst and also as a sorbent for the degradation products of poly (vinyl chloride). In addition to red mud, other catalysts like $\gamma$-$Fe_2O_3$ and silica alumina were employed in the experiments for comparison purpose. The dechlorination ability was investigated in two phases, namely, liquid phase contact, where the catalyst was kept in contact with melted polymer mixtures, and vapour phase contact, where degraded hydrocarbon mixtures from polymer mixtures were in contact with the catalysts. Liquid phase contact yielded better results than vapour phase contact in terms of yield and chlorine content. Red mud could adsorb the HCl but it also led to higher Cl in oil due to reaction between adsorbed HCl and thermal degradation products.

Impregnation of red mud with one or more catalytically active metals is known to increase the reaction efficiency. Fang et al. [109] employed red mud supported Ru catalyst for ammonia decomposition to hydrogen. It was found that acid ($HNO_3$ and HCl) and heat (700 °C) treatment enhanced the catalytic activity of the prepared catalyst. Red mud treated with $HNO_3$ and calcined at 700 °C, supporting 5% Ru showed the highest ammonia conversion percentage of 17%. Ru supported on untreated red mud showed the least activity of 11%. The physical and chemical treatment resulted in higher reducibility of red mud, which subsequently resulted in more dispersive Ru metal on catalyst, thus higher activity. Manh [107] used red mud as support for at least one of the following catalytically active components: Ag, Mn, Cr, Ce, Zr, Ni, Pt, Ru, Cu, V and Co for the conversion of substances including hydrocarbons containing chlorine-, sulphur- and nitrogen-, into less harmful substances and simultaneous colour and odour removal in liquid effluents through wet oxidation. Catalytic wet oxidation introduces air into the wastewater containing pollutants and performs oxidation, decomposition and purification at lower temperature and pressure, in the presence of a catalyst. In the present study the solution containing the active components was precipitated over the milled red mud, followed by washing, drying and calcination. Catalyst were prepared with different compositions and tested for the treatment of certain organic waste containing liquid streams. For e.g. red mud supporting 0.4 wt% $Ag_2O$, 21.2% NiO and 4.4 wt% $CeO_2$ was tested for the treatment of pulp mill effluent and could achieve 84% reduction in colour; for bleach waste from pulp and paper mill, 84% reduction in colour and 50% reduction in chlorinated hydrocarbon content could be obtained; for general effluent from tannery industry 72% reduction in COD; for lime drain effluent from tannery industry, 46% reduction in COD and 95% reduction in sulphide content was obtained and for waste effluent from textile industry 92% reduction in colour was achieved. Further different quantities and composition of catalysts were prepared with the same procedure with promising results for the wet oxidation reaction.

### 3.5. Use of other industrial by-products (having Fe₂O₃) as catalyst

Ferric oxide was regenerated from ferric ion sludge after dewatering, heating at 800 °C for 4 h, and grinding into fine particles size. These regenerated particles were used by Hung and Lin [110] as oxidation catalyst for CO destruction and repression of dioxin formation. Catalytic oxidation is considered to be a good method for reducing the polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCCD/Fs) [111–113]. The major constituent (75%) of the catalyst was $\alpha$-$Fe_2O_3$ (hematite) while other components included smaller percentages of $K_2O$, $Al_2O_3$, $Na_2O$, and $V_2O_5$ etc. The destruction and removal efficiency of three chlorinated compounds namely, chlorobenzene, 2,4-dichlorophenol and trichloroflouroethane was determined. In addition a waste solvent consisting of a mixture of chlorinated (10%) and non-chlorinated compounds (90%) was incinerated to examine the dioxin reducing capacity of the catalyst. The level of CO destruction was found to increase sharply (from 30 to 70%) on addition of the catalyst at 500 °C. The efficiency further increased with the increasing temperature and finally reached the highest (98–100%) at 850 °C. The mechanism of CO oxidation is described by the presence and discharge of the lattice oxygen in $Fe_2O_3$. In the two step oxidation mechanism suggested by Mars and Van Krevelen in 1954 [114], firstly CO is oxidized by the surface oxygen bound to the metal oxide lattice i.e. lattice oxygen. This creates an oxygen vacancy, and the neighboring metal ion gets reduced to a lower oxidation state. The dioxygen of the gaseous phase then reoxidizes the surface metal atom in the second step.

$$CO + O_{lattice} \rightarrow CO_{2,ads} + * \text{ (oxygen vacancy)}$$

$$CO_{2,ads} \rightarrow CO_2 \text{ (g)}$$

$$\tfrac{1}{2}O_2 + * \rightarrow O_{lattice}$$

Ferric oxide is an n-type semiconductor material, which means that it has a net negative charge due to excess of electrons. Examples of some other n-type oxides include $TiO_2$, $V_2O_5$, CoO and $Cr_2O_3$. CO oxidation over such oxides, involves the initial reaction of CO with the lattice oxygen to give surface carbonate and releasing $2e^-$ that are used to reduce the metal ions.

$$CO + 2O^{2-} \rightarrow CO_3{}^{2-} + 2e^-$$
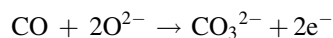
Completion of the catalytic cycle and regeneration of the metal oxide surface takes place by the decomposition of carbonate and metal reoxidation with oxygen. This cycle of lattice oxygen removal followed by its replenishment is referred to as the interfacial process [115].

$$2CO_3{}^{2-} \rightarrow 2CO_2 + 2O^{2-}$$
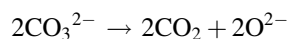
The catalytic activity of any metal oxide (MO) for oxidation of CO depends largely on its tendency to lose an oxygen atom. In oxygen environment the reaction might take place in oxidation–reduction cycle wherein the reduced metal can be reoxidized to the metal oxide. The reaction takes place in two steps.

$$MO + CO \rightarrow M + CO_2$$

$$M + \tfrac{1}{2}O_2 \rightarrow MO$$
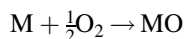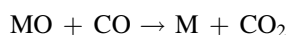
The studies done on CO oxidation with $Fe_2O_3$ have shown that $Fe_2O_3$ nano particles (3–5 nm particle size) perform better than the non-nano oxide powders and also at a lower (by 100 °C) onset temperature [34]. The oxidation reaction over the catalyst takes place by the following reaction:

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$
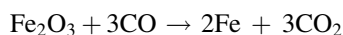
The low onset temperature has been attributed to the presence of FeOOH component in the nanoparticles catalyst, which has a weaker Fe–O bond that is easier to break than that of $\alpha$-$Fe_2O_3$. Scire et al. [116] found that the addition of group IB metals (Au, Ag, Cu) to $Fe_2O_3$ reduced the temperature required to complete the catalytic combustion of volatile organic compounds (VOC) in comparison to pure $Fe_2O_3$. This is explained by the ability of the IB metal to weaken the Fe–O bond located near the metal thus making the lattice oxygen more mobile. The metal with larger size is able to cause greater lattice distortion.

$Fe_2O_3$ supported Au is also an effective catalyst for CO oxidation at low temperatures [117]. In addition to acting as a support material, $Fe_2O_3$ also plays an important part in the catalytic process. The combination of Au + $Fe_2O_3$ was shown to give a synergistic effect.

Cao et al. [118] employed mesoporous CuO-$Fe_2O_3$ composite catalysts for the oxidation of carbon monoxide at low temperatures. The CuO-$Fe_2O_3$ composite having CuO content ranging from 0 to 50 mol% and calcined at 300 °C was tested for its activity at different temperatures up till 300 °C. The highest activity (~100%) was obtained for the catalyst composite having 15% CuO and the highest surface area of 299 m²/g at a temperature of 110 °C. The activity of pure $Fe_2O_3$ was found to be quite low. The reason for higher activity of the CuO-$Fe_2O_3$ composite was attributed to the "wormhole" like structure of the mesopores along with a narrow pore size distribution and high BET surface area.

Radwan [119] studied the effect of doping of rare earth oxides ($Sm_2O_3$ and $Y_2O_3$) on the catalytic properties of $Fe_2O_3$. It was found out that doping led to an increase of the catalytic activity of $Fe_2O_3$ towards CO oxidation with $O_2$ primarily due to the increase in surface area, decrease in crystallinity and particle size. The enhancement of creation of oxygen vacancies in materials doped with $Sm_2O_3$ and $Y_2O_3$ and the preferential adsorption of CO on $Fe_2O_3$ resulted in the net activity increase.

## 4. Conclusion

Red mud offers a wide field of application for catalytic reactions like hydrogenation, hydroliquefaction, oxidation, etc. However, in its natural form, the performance is low compared with iron oxides and the available commercial catalysts, which show efficiency greater that 90%. However, some modifications

can be carried out to improve the performance of red mud as summarized below.

- In addition to the surface area, other properties of red mud like composition of activity enhancing constituents (e.g. Fe and Ti content), sintering agents (Na, Ca etc.), phase of metal oxide present (e.g. anatase $TiO_2$, rutile $TiO_2$ etc.) and particle size also play a role in deciding the catalytic potential. The presence of higher percentage of $Fe_2O_3$ and $TiO_2$ in the catalytically active phase and lower percentage of sintering agents like $Na_2O$ and $CaO$ is desirable.

- Activity can be enhanced via physical and chemical treatments like acid activation, sulphidation, calcination, reduction etc. Such treatments increase the catalytic activity mainly by increasing the surface area of the material or by converting the catalytic species into a more active form. For e.g. reduction of iron oxide to metallic iron is preferred for the reduction of nitrogen oxides.

- Addition of certain materials to the red mud can help improve the activity by synergistic effect. For example the addition of $TiO_2$ or tin in presence of $CS_2$ or in case of oxidation reactions by doping $Fe_2O_3$ with certain metal oxides like $Sm_2O_3$ and $Y_2O_3$ that lead to an increase in the concentration of active sites formed by oxygen vacancy of $Sm_2O_3$ and $Y_2O_3$. Consequently the activity of the material increases. Thus the synergistic effects of various potential additives like $TiO_2$ need to be identified. Naturally occurring cheap sources having $TiO_2$ may be added to red mud to enhance its activity.

- Performance of red mud may also be increased by impregnating it with metals like Cu, Au, Cr etc. where in addition to acting as a support material, it also contributes to the catalytic activity. In addition to providing stability and resistance to the metal catalyst, it may act as an active support providing oxygen in the oxidation reactions. Metal loading possibly from a cheap source like high metal containing wastes, with metals such as Cr or Cu, may be done. Supporting Au particles on red mud for CO oxidation or Cu on red mud for NO reduction can help improve the activity. Loading of metals on red mud can help achieve the desired reaction at lower temperature. For instance the presence of group IB metals decrease the temperature required for the catalytic combustion of VOC on $Fe_2O_3$ catalyst.

The conversion results can be improved by enhancing the catalytic activity of red mud, by a combination of the above mentioned points. In addition, studies on the mechanism, activation, deactivation and lifetime of the red mud catalyst needs to be undertaken.

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